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RECERTIFICATION OF STANDARD REFERENCE MATERIAL (SRM) 1649, URBAN DUST, FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

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The National Institute of Standards and Technology (NIST) recently issued SRM 1649a, Urban Dust, with certified and reference values for 44 polycyclic aromatic hydrocarbons (PAHs). This material is a recertification of SRM 1649 which was issued in 1982 with certified values for only five PAHs. The PAHs were determined using the following analytical techniques: (1) reversed-phase liquid chromatography with fluorescence detection (LC-FL) for analysis of the total PAH fraction, (2) reversed-phase LC-FL for analysis of isomeric PAH fractions isolated by normal-phase LC (*i.e.*, multidimensional LC), and (3) gas chromatography/mass spectrometry (GC/MS) for analysis of the PAH fraction using three different stationary phases, each with different selectivity for PAH separations. The results from the different techniques are compared and discussed. SRM 1649a is currently the most extensively characterized environmental matrix SRM with respect to PAH constituents.

Keywords: Certified Reference Materials (CRMs); gas chromatography/mass spectrometry (GC/MS); liquid chromatography; polycyclic aromatic hydrocarbons (PAHs); Standard Reference Materials (SRMs)

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INTRODUCTION

For nearly two decades the National Institute of Standards and Technology (NIST) has been involved in the development of Standard Reference Materials (SRMs) for the determination of polycyclic aromatic hydrocarbons (PAHs) in natural matrix environmental samples such as fossil fuels [1, 2], air and diesel particulate material [3, 4], coal tar [5], sediment [6, 7], and mussel tissue [8, 9]. Several papers have reviewed and summarized the development of the environmental matrix SRMs for the determination of PAHs [10–13]. There are currently several modes for certification of SRMs at NIST [14, 15]; however, the typical mode used for certification of these natural matrix SRMs for organic contaminants has been the analysis of the material using two or more independent analytical techniques. The results of these multiple technique analyses, if in agreement, are used to determine the "certified" concentrations for the measured analytes. The requirement for using two or more analytical techniques is based on the assumption that the agreement of the results from the independent methods minimizes the possibility of biases within the analytical methods. When results are obtained from only one analytical technique, the concentrations are typically reported as reference values (previously denoted as noncertified values) and are considered as a best estimate of the true value where all known or suspected sources of bias have not been fully investigated by NIST.

The first particle-based natural matrix material developed by NIST for organic contaminants was SRM 1649, Urban Dust/Organics, which was issued in 1982 with certified concentration values for five PAHs (fluoranthene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*ghi*]-perylene, and indeno[1,2,3-*cd*]pyrene) and noncertified concentration values for nine additional PAHs [3, 16]. The certified values for these five PAHs were based on the combined results of analyses by two analytical techniques, gas chromatography with flame ionization detection (GC-FID) and reversed-phase liquid chromatography with fluorescence detection (LC-FL). The values reported for the remaining nine PAHs were based on results from only one analytical technique (*i.e.*, either GC-FID or LC-FL). The relative uncertainties associated with the certified values ranged from a low of 7% (fluoranthene) to a high of 24% (benzo[*ghi*]perylene) with the remaining three PAHs at

12% to 17%, which were considered adequate for the first particle-based matrix SRM.

Even though SRM 1649 had only a limited number of certified values for PAHs, it has been used extensively during the past 17 years as a quality control material and for validation of new analytical methods for PAHs. Several papers report using SRM 1649 for quality assurance in the analysis of air particulate [17, 18], sediment [19] and tobacco smoke samples [20]. SRM 1649 has been used extensively for the development and validation of alternative extraction procedures for PAHs such as supercritical fluid extraction [21–25], ultrasonic extraction [26], pressurized fluid extraction [27], and microwave-assisted solvent extraction [28]. Elsaid *et al.* [29] used SRM 1649 to validate the use of laser-excited Shpol'skii spectrometry for the determination of PAHs on particulate matter.

SRM 1649 has also been characterized extensively for compounds and properties that were not determined at NIST in the original certification measurements. Because of the availability of gram quantities of air particulate matter, SRM 1649 has been used by several groups for the development of bioassay-directed fractionation schemes to identify the compounds responsible for the mutagenic activity in ambient air particulate extracts. Lewtas and coworkers [30] separated the extract from SRM 1649 into six compound fractions by acid-base partitioning and silica gel column chromatography and reported recoveries of both mass and mutagenicity of greater than 80%. Sparacino *et al.* [31] focused on the analysis of the acid fraction isolated from SRM 1649, and they were the first to report the presence of the chlorinated fungicide, dichlorophen, which was an artifact from the sampling bags. Durant *et al.* [32] later quantified the amount of dichlorophen in SRM 1649 as 1400 mg/kg ± 20 mg/kg. Gundel *et al.* [33] developed a fractionation scheme to isolate polar organic constituents from air particulate matter using SRM 1649 and provided both chemical characterization and mutagenic activity for SRM 1649 [34]. Zinbo *et al.* [35] used SRM 1649 to validate the development of a fractionation procedure for bioassay-directed chemical analysis of ambient air particulate extracts.

In the late 1980's SRM 1649 was used in an international collaborative study of the mutagenicity of complex environmental mixtures in the Ames *Salmonella typhimurium* mutation assay [36–38].

Several participants in this collaborative study reported their bioassay results for SRM 1649 [39–41], and the complete results of this study were used to provide reference values for mutagenic activity to the SRM 1649 Certificate of Analysis [16, 38].

Vincent and coworkers [42, 43] used SRM 1649 to investigate the biological response of ambient air particles. Recently SRM 1649 was characterized extensively using a bioassay-directed fractionation method to separate the extract into chemically-simplified fractions which were then tested for mutagenicity using human cells and analyzed by GC/MS for chemical characterization [32]. In this study Durant *et al.* [32] identified 13 PAHs that accounted for ~15% of the total mutagenicity of the extract with the most important mutagens identified as cyclopenta[*cd*]pyrene, benzo[*a*]pyrene, and benzo[*b*]fluoranthene, which accounted for ~7%, ~4% and ~2%, respectively, of the extract mutagenicity. Of particular interest in the report of Durant *et al.* [32] was the quantification of a large number of PAHs, PAH ketones, PAH quinones, acid anhydrides, coumarins, and other compounds that had not previously been reported in SRM 1649.

A number of researchers have reported the concentrations of other classes of compounds in SRM 1649. Helmig *et al.* [44] first reported the presence of 2- and 4-nitrodibenzopyranones in SRM 1649. Reddy and Quinn [45] reported concentrations of benzothiazole, 2-hydroxybenzothiazole, and 2-(4-morpholino)benzothiazole in SRM 1649 as markers for environmental inputs from crumb rubber material (shredded automobile tires). In 1983 Nestrick *et al.* [46, 47] first reported concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), primarily tetrachlorodibenzo-*p*-dioxin congeners, in SRM 1649 and suggested that this material be used as a reference material for dioxin measurements because no air particulate reference materials were available for these measurements. Other groups [48, 49] later reported additional concentrations of PCDDs and polychlorinated dibenzofurans.

The examples described above illustrate the wide range of uses of SRM 1649 and the need to provide certified or reference values for additional PAHs as well as other analytes and properties. Because there is still a considerable supply of SRM 1649 available even after 17 years, recertification of SRM 1649 was undertaken using the current analytical approach for the measurement of PAHs. Since SRM 1649

was first issued in 1982, NIST has developed and implemented improved analytical methods for the measurement and certification of a significantly greater number of PAHs in environmental matrix SRMs [7]. The goals of the recertification of SRM 1649 were: (1) to provide an increased number of certified concentrations for PAHs and other analytes (see below), (2) to reduce the uncertainties associated with the certified concentrations for the PAHs, and (3) to assess the stability of previously measured analytes after nearly 17 years. The recertified air particulate material has been issued as SRM 1649a, Urban Dust [50]. The analytical approach for the recertification measurements for the PAHs consisted of solvent extraction with different solvents, using both Soxhlet extraction and pressurized fluid extraction (PFE), followed by measurement of the PAHs in the extract using the following analytical techniques: (1) reversed-phase liquid chromatography with fluorescence detection (LC-FL) for analysis of the total PAH fraction, (2) reversed-phase LC-FL for analysis of isomeric PAH fractions isolated by normal-phase LC (*i.e.*, multi-dimensional LC), and (3) gas chromatography/mass spectrometry (GC/MS) for analysis of the PAH fraction using three different stationary phases, each with different selectivity for PAH separations (*i.e.*, 5% phenyl-substituted methylpolysiloxane, 50% phenyl-substituted methylpolysiloxane, and smectic liquid crystalline stationary phases). The results from these techniques were combined to provide certified concentrations for 22 PAHs and reference concentrations for an additional 23 PAHs [50]. The relative uncertainties associated with the certified concentrations in SRM 1649a ranged from a low of 2% to a high of 24% with most of the uncertainties in the 5% to 10% range. This paper describes the analytical approach and compares the results from the various techniques used for the measurement of PAHs as part of the recertification of SRM 1649a.

EXPERIMENTAL METHODS

Sample Collection and Preparation

SRM 1649a was prepared from atmospheric particulate material collected in the Washington, DC area in 1976–77 using a baghouse

specially designed for the purpose [16, 51]. The particulate material was collected over a period in excess of 12 months, and therefore represents a time-integrated sample. While the sample is not intended to be representative of the area in which it was collected, it should generally typify atmospheric particulate matter obtained from an urban area. The particulate material was removed from the baghouse filter bags by a specially designed vacuum cleaner and combined into a single lot. This lot was passed through a 125 μm (120 mesh) sieve to remove bag fibers and other extraneous materials. The sieved material was then thoroughly mixed in a V-blender. The material was originally bottled in 10 g units; prior to the recertification measurements, the particulate material was mixed again and rebottled in 5 g units.

Analytical Approach

The general approach used for the determination of PAHs in SRM 1649a was similar to that reported for the recent certification of several environmental matrix SRMs [7, 9]. This approach consisted of Soxhlet extraction and PFE using different solvents followed by analysis of the extract using gas chromatography/mass spectrometry on different stationary phases and reversed-phase liquid chromatography with fluorescence detection. The details of each technique are provided below and summarized graphically in Figure 1.

Gas Chromatography/Mass Spectrometry Analyses

Five sets of GC/MS results, designated as GC/MS (I), GC/MS (II), GC/MS (III), GC/MS (IV) and GC/MS (Sm), were obtained using three columns with different selectivities for the separation of PAHs. For GC/MS (I) analyses, duplicate subsamples of 1 g from 10 bottles were Soxhlet extracted for 20 h with dichloromethane (DCM). The concentrated extract was passed through an aminopropylsilane SPE cartridge and eluted with 2% DCM in hexane. The PAH fraction was then isolated from the extract using normal-phase LC on a semi-preparative aminopropylsilane column. The PAH fraction was then analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a 5% (mole fraction) phenyl-substituted methylpolysiloxane phase (0.25 μm film thickness) (DB-5 MS, J and W Scientific,

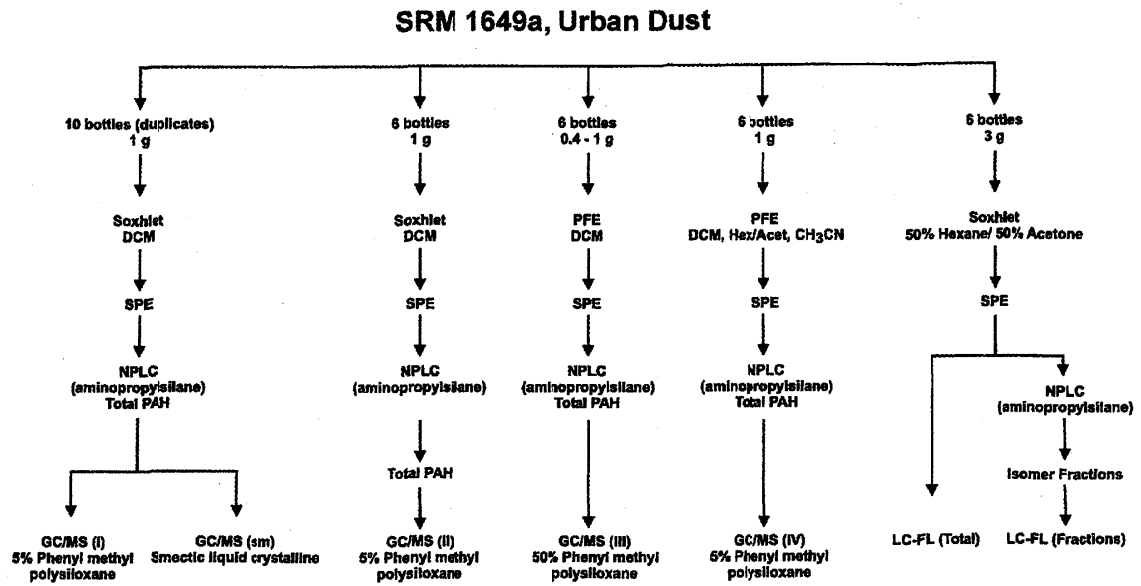

FIGURE 1 Analytical scheme for the certification of SRM 1649a.

Folsom, CA). The GC/MS (II) analyses consisted of subsamples from six bottles analyzed as a second sample set using the same preparation and analysis procedures as described for GC/MS (I). Two additional sets of GC/MS results for a limited number of PAHs, designated as GC/MS (III) and GC/MS (IV), were obtained using PFE followed by GC/MS. For the GC/MS (III) analyses subsamples of 0.4 g to 1 g from six bottles were extracted with DCM using PFE, as described by Schantz *et al.* [27], the extracts were processed as described above for GC/MS (I), followed by GC/MS analysis on a 50% (mole fraction) phenyl-substituted methylpolysiloxane stationary phase (0.25 mm i.d. × 60 m, 0.25 μm film thickness) (DB-17MS, J and W Scientific, Folsom, CA). For GC/MS (IV) analyses two subsamples of 1 g each were extracted with each of three different solvents (DCM, acetonitrile, and 50% hexane/50% acetone mixture) using PFE; the extracts were processed and analyzed by GC/MS on the 5% phenyl-substituted methylpolysiloxane stationary phase described above for GC/MS (I). The GC/MS (Sm) results were obtained by analyzing selected sample extracts from the GC/MS (I) set on a 0.2 mm i.d. × 25 m (0.15 μm film thickness) smectic liquid crystalline phase (SB-Smectic, Dionex, Lee Scientific Division, Salt Lake City, UT). For all of the GC/MS measurements, selected perdeuterated PAHs were added to the particulate matter prior to solvent extraction for use as internal standards for quantification purposes (see Tab. I).

For the GC/MS (I) and (II) analyses the temperature program was as follows: 1 min hold at 100°C followed by rapid ramp (60°C/min) to 150°C, then temperature programmed at 2°C/min to 300°C. For GC/MS (III) and (IV) analyses the temperature program was as follows: 1 min hold at 60°C followed by rapid ramp (45°C/min) to 150°C (2 min hold), then temperature programmed at 2°C/min to 290°C. Injections for all GC/MS methods were on-column. For GC/MS (Sm) analyses the temperature program was as follows: 1 min hold at 60°C followed by rapid ramp (40°C/min) to 150°C, then temperature programmed at 3°C/min to 270°C with a hold for 130 min.

The homogeneity of SRM 1649a was assessed by analyzing duplicate samples of 1 g from 10 randomly selected bottles. Samples were extracted, processed, and analyzed as described above for the GC/MS (I). No statistically significant differences between bottles were observed for the PAHs at the 1 g sample size. Recent analyses of

TABLE I Comparison of internal standards used in the LC-FL and GC/MS methods

	LC (Total)	*LC (Fraction)*	*GC/MS* (I) *and (Sm)*	*GC/MS* (II)	*GC/MS* (III) *and* (IV)
Phenanthrene	Phen-d_{10}		Phen-d_{10}	Phen-d_{10}	Phen-d_{10}
Anthracene	Phen-d_{10}		Phen-d_{10}	Phen-d_{10}	Phen-d_{10}
Fluoranthene	Fluor-d_{10}		Fluor-d_{10}	Pyrene-d_{10}	Fluor-d_{10}
Pyrene	Fluor-d_{10}		Fluor-d_{10}	Pyrene-d_{10}	Fluor-d_{10}
Benz[*a*]anthracene	B[*a*]A-d_{12}	B[*a*]A-d_{12}	B[*a*]A-d_{12}	B[*a*]A-d_{12}	B[*a*]A-d_{12}
Chrysene	B[*a*]A-d_{12}	B[*a*]A-d_{12}	B[*a*]A-d_{12}	B[*a*]A-d_{12}	B[*a*]A-d_{12}
Triphenylene	Trip-d_{12}	Trip-d_{12}	B[*a*]A-d_{12}	B[*a*]A-d_{12}	B[*a*]A-d_{12}
Benzo[*b*]fluoranthene	B[*a*]A-d_{12}		B[*e*]P-d_{12}	B[*k*]Fl-d_{12}	B[*a*]P-d_{12}
Benzo[*k*]fluoranthene	Per-d_{12}		B[*e*]P-d_{12}	B[*k*]Fl-d_{12}	B[*a*]P-d_{12}
Benzo[*e*]pyrene			B[*e*]P-d_{12}	B[*a*]P-d_{12}	B[*a*]P-d_{12}
Benzo[*a*]pyrene	Per-d_{12}		B[*e*]P-d_{12}	B[*a*]P-d_{12}	B[*a*]P-d_{12}
Perylene	Per-d_{12}		B[*e*]P-d_{12}	B[*a*]P-d_{12}	Per-d_{12}
Anthanthrene	Per-d_{12}	B[*ghi*]P-d_{12}	DB[*a*, *h*]A-d_{14}		
			B[*ghi*]Per-d_{12}[a]		
Benzo[*ghi*]perylene	Per-d_{12}	B[*ghi*]Per-d_{12}	DB[*a*, *h*]A-d_{14}	B[*ghi*]Per-d_{12}	B[*ghi*]Per-d_{12}
Indeno[1.2,3-*cd*']pyrene	Per-d_{12}	B[*ghi*]Per-d_{12}	DB[*a*, *h*]A-d_{14}	B[*ghi*]Per-d_{12}	B[*ghi*]Per-d_{12}
Dibenz[*a*, *j*]anthracene		DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}
Dibenz[*a*, *c*]anthracene		DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}
Dibenz[*a*, *h*]anthracene		DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}
Pentaphene		DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}
Benzo[*b*]chrysene		DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}
Picene		DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}	DB[*a*, *h*]A-d_{14}

[a] Internal standard for GC/MS (Sm) only.

subsamples of 1 mg to 400 mg show no significant differences in the PAH concentrations [52].

Liquid Chromatography-Fluorescence Detection Analyses

Two sets of LC-FL results, designated as LC-FL (Total) and LC-FL (Fraction), were used in the certification process. Subsamples of 3 g from six bottles were Soxhlet extracted for 20 h using 50% hexane/50% acetone (volume fractions). The extracts were concentrated and then processed through an aminopropylsilane solid phase extraction (SPE) cartridge to obtain the total PAH fraction. Approximately one third of this fraction was analyzed as the total PAH fraction; the second portion of the total PAH fraction was then fractionated on a semi-preparative aminopropylsilane column to isolate isomeric PAH fractions as described previously [3, 5, 53]. Three PAH isomer fractions were collected: four aromatic ring *cata*-condensed isomers (228 molecular weight), five aromatic ring *cata*-condensed isomers (278 molecular weight), and six aromatic ring *peri*-condensed isomers (276 molecular weight). The total PAH fraction and the isomeric PAH fractions were analyzed using both 3 μm and 5 μm particle-size polymeric octadecylsilane (C_{18}) columns (4.6 mm i.d. × 15 cm, 3 μm particle size, ChromSpher PAH, Chrompack, Middelburg, The Netherlands and 4.6 mm i.d. × 25 cm, Hypersil-PAH, Keystone Scientific, Inc., Bellefonte, PA) with wavelength-programmed fluorescence detection [3, 5, 7]. The excitation and emission wavelengths and the times at which the wavelengths were changed are indicated on each of the LC-FL chromatograms. For all of the LC-FL measurements, selected perdeuterated PAHs were added to the particulate matter prior to solvent extraction for use as internal standards for quantification purposes (see Tab. I).

For the analysis of the total PAH fraction using the 5 μm column, the chromatographic conditions were as follows: linear gradient from 50% acetonitrile in water to 100% acetonitrile in 50 min at 1.5 mL/min; hold at 100% for 10 min. For the analysis of the total PAH fraction using the 3 μm column, the chromatographic conditions were as follows: linear gradient from 50% acetonitrile in water to 100% acetonitrile in 15 min at 2 mL/min; hold at 100% for 5 min. For the

analysis of the four aromatic ring PAH fraction the 5 μm column was used with the following chromatographic conditions: isocratic at 70% acetonitrile in water for 20 min at 1.5 mL/min; then linear gradient to 100% acetonitrile in 15 min. For the analysis of the six aromatic ring PAH fraction the 5 μm column was used with the following chromatographic conditions: isocratic at 80% acetonitrile in water for 5 min at 1.5 mL/min; then linear gradient to 100% acetonitrile in 15 min; hold 10 min. For the analysis of the five aromatic ring PAH fraction a different 5 μm polymeric C_{18} column with a high phase loading ($r_{TBN/BaP} = 0.46$) [54, 55] was used with the following chromatographic conditions: isocratic at 90% acetonitrile in water for 10 min at 1.5 mL/min; then linear gradient to 100% acetonitrile in 2 min, hold at 100% acetonitrile for 13 min. The column temperature was held at 26°C for all the LC analyses except for the 278 molecular weight isomer fraction which was held at 32°C.

Quality Assurance Procedures

For all of the GC/MS and LC/FL analyses, a blank sample (*i.e.*, solvent with the internal standards added) was run through the complete process. No significant levels of PAHs were found in the blanks, and the concentrations reported from each method have no blank correction. All GC/MS and LC/FL analyses were performed with duplicate injections of the samples and the mean reported. Because the original certified values for SRM 1649 were available, the samples analyzed also served as a control material for the analyses.

Conversion to Dry-mass Basis

The results for the constituents in SRM 1649a are reported on a dry-mass basis; however, the material "as received" contains residual moisture. The amount of moisture in SRM 1649a was determined by measuring the mass loss after freeze-drying subsamples of 1.6 g to 2.5 g for five days at 1 Pa with a − 10°C shelf temperature and a − 50°C condenser temperature. The moisture content in SRM 1649a at the time of the certification analyses was 1.23% ± 0.07% (95% confidence level).

RESULTS AND DISCUSSION

Analytical Approach for Certification

The analytical approach used for the determination of PAHs in SRM 1649a was based on the use of two or more analytical methods that are chemically independent, *i.e.*, there are significant differences in the various steps in the analytical process (extraction, cleanup, separation, and detection). For the recertification of SRM 1649a, results were used from seven different sets of measurements which incorporated various differences in extraction and cleanup followed by separation and detection using the following techniques: (1) reversed-phase liquid chromatography with fluorescence detection (LC-FL) for analysis of the total PAH fraction, (2) reversed-phase LC-FL for analysis of isomeric PAH fractions isolated by normal-phase LC, and (3) gas chromatography/mass spectrometry (GC/MS) for analysis of the PAH fraction using three different stationary phases with different selectivity for PAH separations. The analytical scheme for the recertification of SRM 1649a is illustrated in Figure 1. The original recertification approach was designed to provide five sets of results [GC/MS (I) GC/MS (II), GC/MS (Sm), LC-FL (Total) and LC-FL (Fractions)]; however, during the certification analyses two new improvements in the analytical procedures were implemented to provide additional results for selected PAHs: (1) PFE was used as an alternative solvent extraction technique [GC/MS (III) and GC/MS (IV)] and (2) a 50% phenyl methylpolysiloxane stationary phase was used to provide separation of selected PAH isomers [GC/MS (III)].

Comparison of Results Among Analytical Methods

The certification of SRM 1649a provided the opportunity to compare several different analytical methods and to investigate any differences among the methods. The results of the analyses using the various techniques are summarized in Table II for 23 PAHs. Even though the results for only a limited number of PAHs from GC/MS (III) and GC/MS (IV) were used in the assignment of the certified values, the results for the other PAHs from these two methods are provided in Table II to demonstrate further the comparability of results among the seven methods.

TABLE II Summary of analytical results from different methods for the determination of PAHs in SRM 1649a, Urban Dust

Compound	Concentration (mg/kg dry-mass basis)[a,b]													
	GC/MS (I) (*DB-5*)		*GC/MS* (II) (*DB-5*)		*GC/MS* (III) (*DB-5*)		*GC/MS* (IV) (*DB*-17)		*GC/MS* (*Sm*) (*SB-Smectic*)		*LC-FL* (*Total*)		*LC-FL* (*Fractions*)	
Phenanthrene	4.03	(0.07)	3.89	(0.04)	4.41	(0.12)*	3.98	(0.07)*	4.16	(0.08)	4.49	(0.20)[c]		
Anthracene	0.351	(0.022)	0.492	(0.021)	0.426	(0.017)*	0.412	(0.006)*	0.412	(0.013)	0.472	(0.036)[c]		
Fluoranthene	6.59	(0.11)	6.32	(0.05)	6.45	(0.27)*	6.39	(0.08)*	6.46	(0.08)	6.42	(0.33)[c]		
Pyrene	5.50	(0.28)	5.05	(0.04)	5.38	(0.08)*	5.25	(0.05)*	5.33	(0.07)	5.29	(0.42)[c]		
Chrysene									3.03	(0.05)	3.26	(0.04)*	3.07	(0.02)
Benz[*a*]anthracene	2.21	(0.05)	2.14	(0.00)	2.25	(0.11)*	2.42	(0.03)*	2.24	(0.03)	2.14	(0.03)*	2.25	(0.02)
Triphenylene									1.32	(0.09)	0.81	(0.02)*	1.40	(0.01)
Chrysene/Triphenylene[d]	4.25	(0.06)[d,*]	4.17	(0.07)[d,*]	4.72	(0.22)[d,*]	4.51	(0.07)[d,*]						
Benzo[*b*]fluoranthene							6.48	(0.25)	5.83	(0.08)	7.04	(0.31)		
Benzo[*j*]fluoranthene							1.02	(0.02)	1.89	(0.03)				
Benzo[*b+j*]fluoranthene[e]	7.62	(0.10)[e,*]	7.16	(0.09)[e,*]	7.45	(0.21)[e,*]								
Benzo[*k*]fluoranthene	1.89	(0.06)	1.90	(0.04)	1.87	(0.04)*	1.94	(0.04)	1.92	(0.03)	1.92	(0.03)		
Benzo[*a*]fluoranthene	0.427	(0.018)	0.424	(0.022)	0.438	(0.004)*	0.416	(0.005)*	0.377	(0.021)				
Benzo[*e*]pyrene	3.11	(0.03)	2.91	(0.07)	3.00	(0.05)*	3.26	(0.04)*	3.24	(0.04)				
Benzo[*a*]pyrene	2.44	(0.03)	2.49	(0.04)	2.39	(0.01)*	2.57	(0.06)*	2.56	(0.07)	2.55	(0.12)		
Perylene	0.646	(0.014)	0.617	(0.012)	0.648	(0.004)*	0.700	(0.016)*	0.610	(0.021)	0.642	(0.007)[c]		
Indeno[1,2,3-*cd*]pyrene	2.46	(0.14)	3.17	(0.06)	3.21	(0.13)	3.44	(0.11)			3.53	(0.09)*	3.62	(0.13)
Benzo[*ghi*]perylene	3.10	(0.16)	4.07	(0.04)	3.72	(0.13)	4.36	(0.11)			3.34	(0.25)*	4.79	(0.16)
Dibenz[*a,j*]anthracene	0.277	(0.013)	0.324	(0.018)	0.303	(0.004)*	0.321	(0.008)	0.320	(0.012)			0.308	(0.011)[c]
Dibenz[*a,c*]anthracene							0.181	(0.010)	0.224	(0.014)			0.195	(0.004)[c]

TABLE II (Continued)

Compound	Concentration (mg/kg dry-mass basis)[a,b] GC/MS (I) (DB-5)	GC/MS (II) (DB-5)	GC/MS (III) (DB-5)	GC/MS (IV) (DB-17)	GC/MS (Sm) (SB-Smectic)	LC-FL (Total)	LC-FL (Fractions)
Dibenz[*a,h*]anthracene				0.265 (0.013)	0.300 (0.027)		0.298 (0.008)[c]
Dibenz[*a,h* + *a, c*]anthracene[f]	0.403 (0.017)[f,*]	0.444 (0.016)[f,*]	0.400 (0.027)[f,*]				
Pentaphene	0.116 (0.006)	0.169 (0.008)	0.144 (0.005)*	0.160 (0.006)	0.144 (0.006)		0.165 (0.008)
Benzo[*b*]chrysene	0.306 (0.017)	0.325 (0.027)	0.331 (0.005)*	0.320 (0.006)	0.307 (0.026)		0.315 (0.009)[c]
Picene	0.421 (0.024)	0.416 (0.018)	0.432 (0.007)*	0.437 (0.008)	0.413 (0.034)		0.445 (0.013)[c]
Anthanthrene	0.508 (0.041)	0.393 (0.031)			0.463 (0.052)	0.458 (0.023)[c]	0.520 (0.026)

[a] Concentrations reported on dry-mass basis; material as received contains approximately 1.2% moisture.
[b] The value in parentheses is the standard deviation of a single measurement.
[c] Value includes results from both the 3 μm and 5 μm particle-size column.
[d] Concentration is the sum of chrysene and triphenylene.
[e] Concentration is the sum of benzo[*b*]fluoranthene and benzo[*j*]fluoranthene.
[f] Concentration is the sum of dibenz[*a,c*]anthracene and dibenz[*a,h*]anthracene.
* Result not used in the determination of the certified value for this compound.

Comparison of Extraction Methods

The seven sets of results represent two different solvent extraction techniques, Soxhlet extraction and PFE, using three different solvents, dichloromethane, hexane/acetone (50:50, volume fraction), and acetonitrile. Recently Schantz *et al.* [27] validated the comparability of PFE and Soxhlet extractions for several environmental matrix SRMs including SRM 1649a. The certification of SRM 1649a and a new sediment material, SRM 1944, New York/New Jersey Waterway Sediment [56], represent the first use of results obtained from PFE and the 50% phenyl methylpolysiloxane phase in the value assignment of an environmental matrix SRM for PAHs. Recently Benner [25] investigated the comparability of supercritical fluid extraction (SFE) to Soxhlet solvent extraction for SRM 1649a and found that recoveries for the higher molecular weight PAHs (*i.e.*, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene) were not comparable, thus SFE was not used as another extraction technique in the recertification of SRM 1649a. The incorporation of additional results using the new PFE technique was initiated to provide more confidence in the value assignment for benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene. Based on the range of the results obtained for these two PAHs using GC/MS (I and II) and LC-FL (2.46 mg/kg to 3.62 mg/kg for indeno[1,2,3-*cd*]pyrene and 3.10 mg/kg to 4.79 mg/kg for benzo[*ghi*]perylene), two additional sets of data [GC/MS (III) and GC/MS (IV)] were obtained using PFE with several solvents. These two additional methods provided values of 3.21 mg/kg and 3.44 mg/kg for indeno[1,2,3-*cd*]pyrene and 3.72 mg/kg and 4.36 mg/kg for benzo[*ghi*]perylene, which were included in the determination of the certified value for these two PAHs (see Tab. II).

Sample cleanup of the solvent extracts consisted of solid phase extraction (SPE) on an aminopropylsilane cartridge followed by either direct analysis [in the case of LC-FL (Total)] or further cleanup using normal-phase LC on a semipreparative aminopropylsilane column to isolate either a total PAH fraction for GC/MS analysis or isomer fractions for LC-FL analysis.

Gas Chromatography/Mass Spectrometry Analyses

The most significant differences in the analytical methods are provided in the final chromatographic separation and detection step using

GC/MS and LC-FL. For the GC/MS analyses the 5% phenyl methylpolysiloxane phase has been a commonly used phase for the separation of PAHs; however, several important PAH isomers are not completely resolved on this phase, *i.e.*, chrysene and triphenylene, benzo[*b*]fluoranthene and benzo[*j*]fluoranthene, and dibenz[*a*, *h*]anthracene and dibenz[*a*, *c*]anthracene. To achieve separation of these isomers, GC/MS analyses were also performed using two other phases with different selectivity, a 50% phenyl methylpolysiloxane phase [57] and a smectic liquid crystalline phase. Both of these phases completely resolve the benzofluoranthene isomers (molecular weight 252) (see Fig. 2B) and dibenzanthracene isomers (molecular weight 278) (only partially resolved on the 50% phenyl phase) (see Fig. 2C); however, only the smectic liquid crystalline phase completely separates the isomeric triphenylene and chrysene (molecular weight 228) (see Fig. 2A). The separations of these three isomer groups on the three columns are illustrated in Figures 2A, 2B, and 2C.

The elution order of the PAHs of interest on the 5% and 50% phenyl methylpolysiloxane phases is similar with only minor differences, *e.g.*, benzo[*j*]fluoranthene elutes after benzo[*k*]fluoranthene among the 252 molecular weight isomer and pentaphene elutes before dibenz[*a*, *c*]anthracene and dibenz[*a*, *h*]anthracene among the 278 molecular weight isomers on the 50% phenyl phase. The smectic liquid crystalline phase provides a very different elution order compared with the two phenyl phases. The GC separation on liquid crystalline phase is based to some extent on the shape of the PAHs, *i.e.*, the more rod-like PAH isomers elute later than the more compact structures [7, 58, 59]. The difference in elution order for the liquid crystalline phase is most pronounced for the 252 molecular weight isomers where the elution order changes from benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, and perylene using the 50% phenyl phase to an elution order of benzo[*a*]fluoranthene, benzo[*j*]fluoranthene, benzo[*b*]fluoranthene, benzo[*e*]pyrene, benzo[*k*]fluoranthene, perylene, and benzo[*a*]pyrene using the liquid crystalline phase. For the 278 molecular weight isomers the elution order is similar but the selectivity (*i.e.*, relative separation of the isomers) is much greater on the liquid crystalline phase. In general the selectivity, as well as the range over which an isomer group elutes, increase slightly from the 5%

MW 228 Isomers

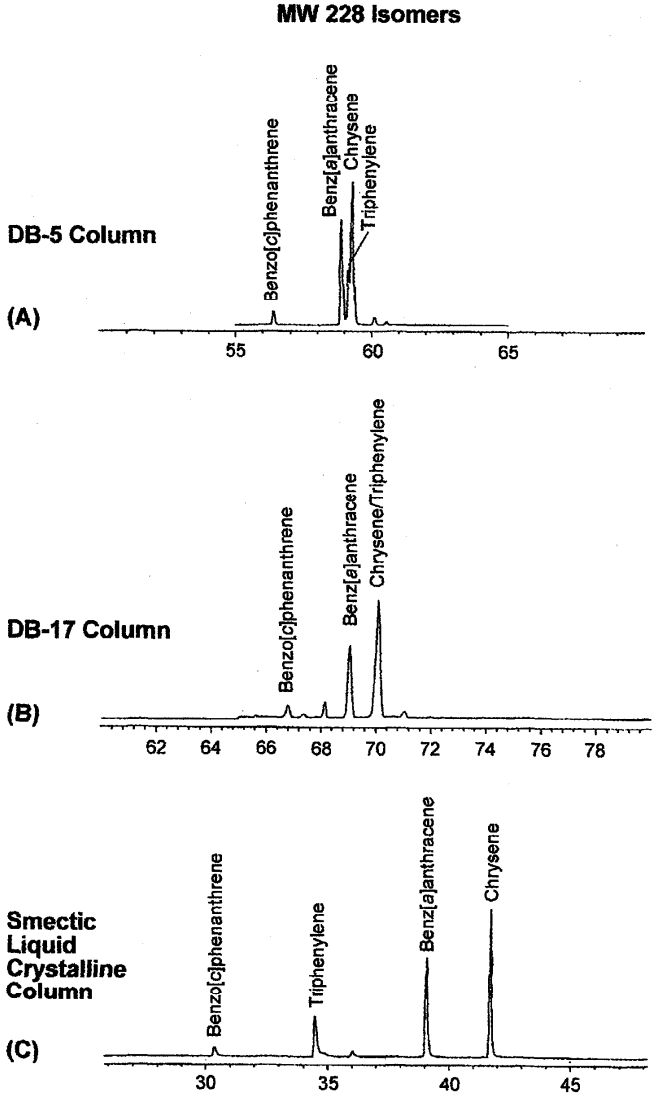

FIGURE 2A GC/MS analysis of the total PAH fraction from SRM 1649a using three stationary phases for the determination of PAH isomers of molecular weight 228: (A) 5% phenyl methylpolysiloxane (DB-5), (B) 50% phenyl methylpolysiloxane (DB-17), and (C) smectic liquid crystalline phase.

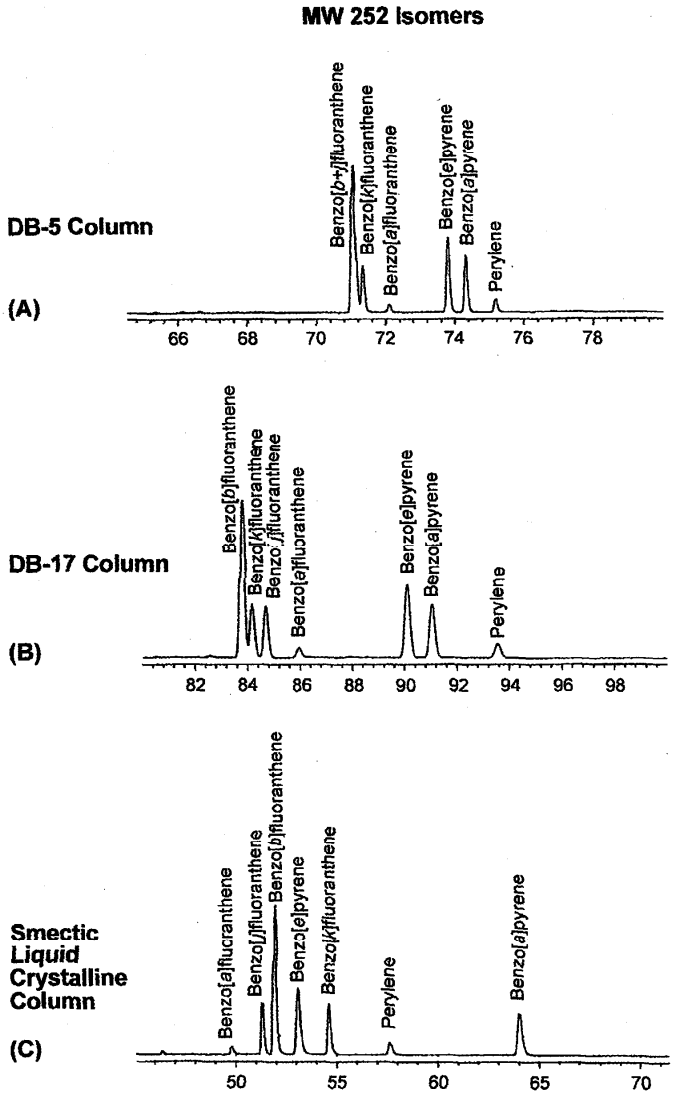

FIGURE 2B GC/MS analysis of the total PAH fraction from SRM 1649a using three stationary phases for the determination of PAH isomers of molecular weight 252: (A) 5% phenyl methylpolysiloxane (DB-5), (B) 50% phenyl methylpolysiloxane (DB-17), and (C) smectic liquid crystalline phase.

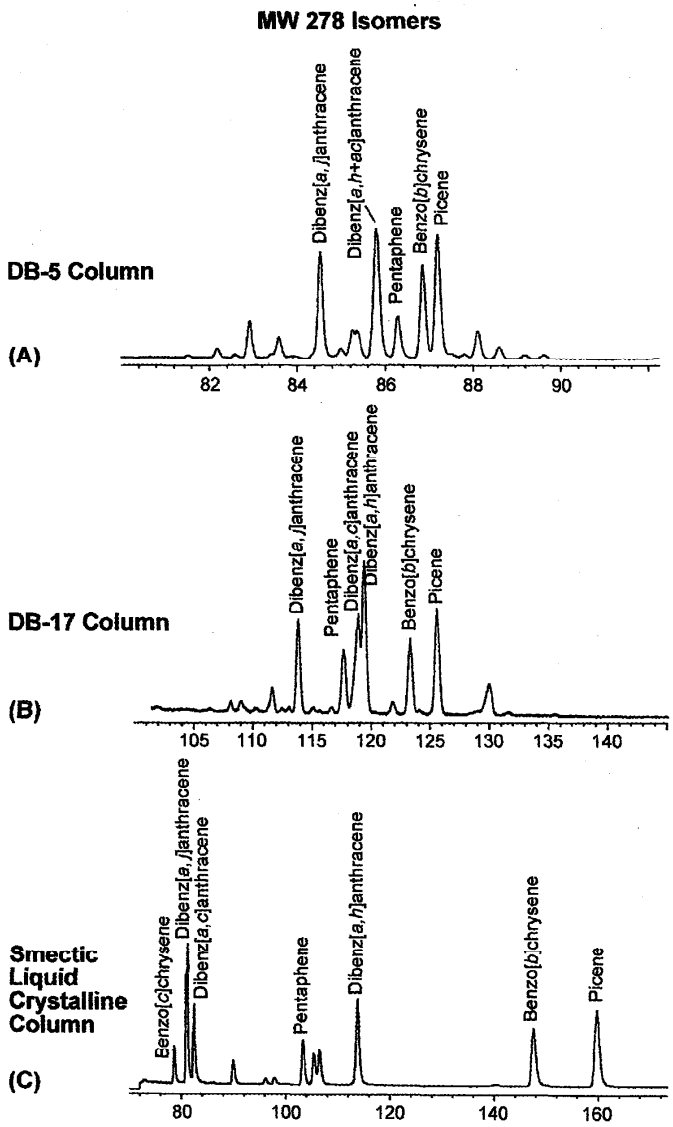

FIGURE 2C GC/MS analysis of the total PAH fraction from SRM 1649a using three stationary phases for the determination of PAH isomers of molecular weight 278: (A) 5% phenyl methylpolysiloxane (DB-5), (B) 50% phenyl methylpolysiloxane (DB-17), and (C) smectic liquid crystalline phase.

phenyl phase to the 50% phenyl phase, but increase significantly for the liquid crystalline phase. For example the elution ranges of the 252 molecular weight isomers on the 5% phenyl, 50% phenyl, and liquid crystalline phase are 4 min, 10 min, and 14 min, respectively (see Fig. 2B). For the 278 molecular weight isomers the elution ranges for the three columns are 3 min, 13 min, and 84 min (see Fig. 2C). The extremely long elution times for the liquid crystalline phase make its use impractical for routine determination of PAHs. However, the unique selectivity of the liquid crystalline phase, and the differences in selectivity of the two phenyl phases provide the necessary independence among the GC/MS methods to justify the use of results from these three columns in the determination of the certified values.

The GC/MS separations of the methylphenanthrene isomers on the three stationary phases are illustrated in Figure 3. On the 5% phenyl methylpolysiloxane phase, the 9-methyl- and 4-methylphenanthrene isomers are only partially resolved, and because the 4-methyl isomer is typically present in environmental samples at lower levels compared to the 9-methyl isomer (see Fig. 3A), this isomer is often difficult to quantify individually; thus the concentration of the 4-methyl- and 9-methylphenathrene isomers are generally reported together [60] as in Table V. The elution order of the five methylphenanthrene isomers is similar on the 5% and 50% phenyl methylpolysiloxane phases with the exception that on the 5% phenyl methylpolysiloxane phase the 4-methyl isomer elutes after the 1-methyl isomer and is completely resolved from the other isomers. The smectic liquid crystalline phase provides a different elution order (3-methyl < 9-methyl < 1-methyl < 2-methyl) with the separation based somewhat on the shape of the isomer. Budzinski *et al.* [61] first reported the use of the liquid crystalline column for the separation and identification of methylphenanthrene and methylanthracene isomers in crude oil and rock extracts. The 2-methylanthracene isomer, which elutes in the midst of the methylphenanthrene isomers on the 5% and 50% phenyl phases, elutes beyond all the methylphenanthrene isomers on the liquid crystalline phase. The quantitative results for the measurement of six methylphenathrene and methylanthracene isomers by the different GC/MS techniques are compared in Table III. Only the results from the 5% phenyl methylpolysiloxane phase [both GC/MS (I) and GC/MS (II)] and the smectic liquid crystalline phase [GC/MS (Sm)]

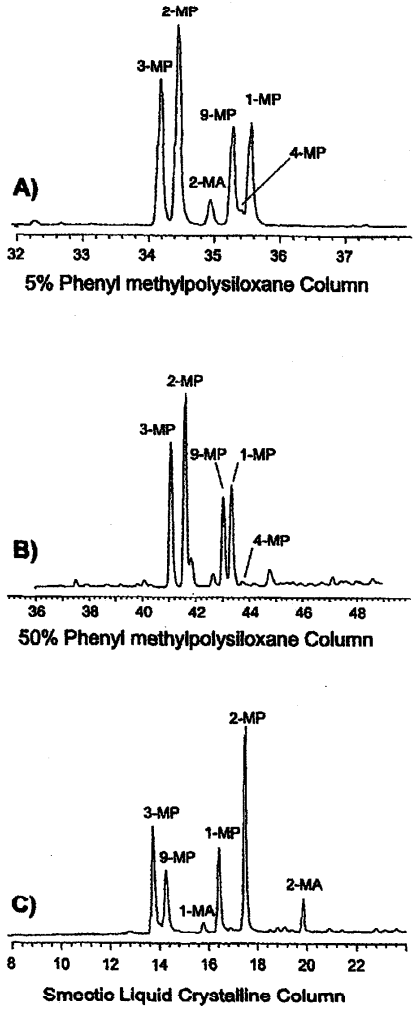

FIGURE 3 GC/MS analysis of the total PAH fraction from SRM 1649a using three stationary phases for the determination of methylphenanthrenes (molecular weight 192): (A) 5% phenyl methylpolysiloxane, (B) 50% phenyl methylpolysiloxane, and (C) smectic liquid crystalline phase.

TABLE III Comparison of results for methylphenanthrene isomers by different GC methods

	Concentration (μg/kg dry-mass basis)[a]							
	GC/MS (I)[b]		*GC/MS* (II)[b]		*GC/MS* (IV)		*GC/MS* (*Sm*)[b]	
1-Methylphenanthrene	342	(27)	346	(25)	364	(23)	408	(20)
2-Methylphenanthrene	678	(33)	666	(45)	704	(42)	850	(30)
3-Methylphenanthrene	464	(17)	488	(33)	501	(28)	552	(34)
4-Methylphenanthrene					64	(5)		
9-Methylphenanthrene	325	(23)	339	(20)	317	(22)	343	(35)
2-Methylanthracene	74	(6)	81	(14)			118	(5)

[a] The value in parentheses is the standard deviation of a single measurement. Note that the concentrations are in μg/kg whereas the concentrations in Tables II, IV, V and VII are in mg/kg.
[b] Results from GC/MS (I), GC/MS (II) and GC/MS (Sm) were used to determine reference value in Table V for these compounds.

were used to assign reference values. However, the results from the 50% phenyl phase are in good agreement with the reference values. SRM 1649a is the first SRM where results from the liquid crystalline phase were used in conjunction with results from the 5% phenyl phase (with results from the 50% phenyl phase used to confirm) to provide reference values for the methylphenanthene isomers. These values were not classified as "certified" because of the lack of sufficient information on the purity of the methylphenanthrene standards used for calibration.

Liquid Chromatography Analyses

In the analysis of complex PAH mixtures obtained from environmental samples, reversed-phase LC-FL typically provides reliable results for only 8–12 major PAHs [62]. To increase the number of PAHs determined by LC-FL, a multidimensional LC procedure was used to isolate and enrich specific isomeric PAHs that could not be measured easily in the total PAH fraction because of interferences, low concentrations, and/or low fluorescence sensitivity or selectivity. This multidimensional procedure, which has been described previously [54], consists of a normal-phase LC separation of the PAHs based on the number of aromatic carbon atoms in the PAH, thereby providing fractions containing only isomeric PAHs and their alkyl-substituted isomers [3, 62]. These isomeric fractions are then analyzed by reversed-phase LC-FL to separate and quantify the various isomers. For the certification of SRM 1649a three isomer fractions were isolated and

analyzed: the four aromatic ring *cata*-condensed PAHs (molecular weight 228), the five aromatic ring *cata*-condensed PAHs (molecular weight 278), and the six aromatic ring *peri*-condensed PAHs (molecular weight 276).

The reversed-phase LC analyses (both total and isomer fractions) were performed using a polymeric C_{18} phase, which provides excellent selectivity for the separation of PAH isomers [62–64]. These LC-FL analyses were performed using a 5 μm particle-size column as described for previous certification measurements [5, 7]; however, we also investigated and implemented the use of a 3 μm particle-size polymeric C_{18} column. Wavelength programmed fluorescence detection was used to provide detection selectivity [3, 5, 7]. The reversed-phase LC analysis of the total PAH fraction using the 5 μm particle-size column with wavelength programmed fluorescence detection for SRM 1649a is shown in Figure 4A. Benzo[*b*]fluoranthene was determined in a second LC-FL analysis of the same total PAH fraction using excitation and emission wavelengths selective for benzo[*b*]fluoranthene instead of the wavelengths used for perylene in the first LC-FL method. A total of 14 PAHs were measured in the LC-FL analysis of the total PAH fraction; however, only results for 9 PAHs were considered sufficiently reliable for use in the assignment of the certified values (see Tab. II). Even though it was possible to measure triphenylene, benz[*a*]anthracene, chrysene, benzo[*ghi*]perylene, and indeno[1,2,3-*cd*]pyrene in the total PAH fraction, the results were considered as questionable because of possible coelution of minor components with either the analyte of interest or the internal standards. The LC-FL analyses of the four, five, and six aromatic ring isomer fractions isolated from the multidimensional LC procedure were used to overcome these limitations (see discussion below).

The total PAH fraction was also analyzed using a 3 μm particle-size polymeric C_{18} column as illustrated in Figure 4B. Using the 3 μm column, the analysis time was reduced to approximately 20 min compared to 60 min for the 5 μm column. Results for 12 PAHs were obtained using the 3 μm column (triphenylene and benzo[*b*]fluoranthene were not determined); however, only results for phenanthrene, anthracene, fluoranthene, pyrene, perylene, and anthanthrene were considered sufficiently reliable for use in the determination of the certified value. It was not possible to quantify benzo[*k*]fluoranthene reliably because

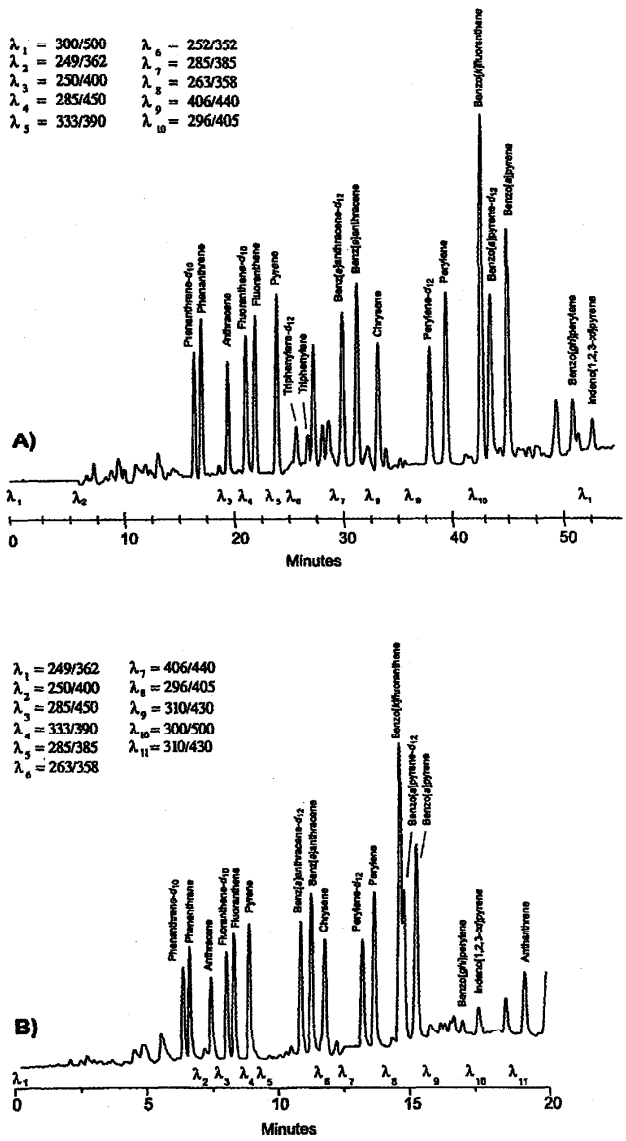

FIGURE 4 Reversed-phase LC-FL analysis of total PAH fraction from SRM 1649a using (A) a 5 µm and (B) a 3 µm particle-size polymeric C_{18} column.

of incomplete separation from benzo[*a*]pyrene-d_{12}, which was added (but not used) as the internal standard. Results for benzo[*a*]pyrene were 37% higher using the 3 μm column as compared to the 5 μm column indicating a possible coelution problem. The 3 μm column was also used for the determination of the 278 molecular weight isomers as described below.

The LC-FL analysis of the four aromatic ring fraction is shown in Figure 5A. The results from the analysis of the isomer fraction differ only slightly (5% and 10%) compared to the total PAH fraction for the determination of chrysene and benz[*a*]anthracene; however, the results for triphenylene in the isomer fraction are significantly higher (70%) (see Tab. II). The large increase in the triphenylene value for the isomer fraction can be attributed to the removal of coeluting interferences with the internal standard, triphenylene-d_{12}, in the total PAH fraction (compare Fig. 4A with 5A). The small decrease in the results for chrysene is probably due to the removal of minor coeluting peak(s) and the small increase in the benz[*a*]anthracene result is probably due to removal of coeluting peaks with the internal standard (benz[*a*]anthracene-d_{12}).

The LC-FL analysis of the six aromatic ring fraction is shown in Figure 5B. The results for indeno[1,2,3-*cd*]pyrene and anthanthrene in both the total and isomer fractions (see Tab. II) were similar (within 2–3%) probably because of the extreme selectivity of the fluorescence excitation and emission wavelengths for these analytes. However, the benzo[*ghi*]perylene result from the total fraction was 30% lower than the isomer fraction result.

The 278 molecular isomers were determined using the approach described previously by Wise *et al.* [31]. The LC-FL analysis of the five aromatic ring *cata*-condensed PAH isomers is shown in Figure 6 using both the 5 μm and the 3 μm columns. Using the 5 μm column several of the isomers, *i.e.*, dibenz[*a,j*]anthracene, dibenz[*a,h*]anthracene, and picene (see Fig. 6A), were not completely resolved from other compounds. For example, dibenz[*a,h*]anthracene is not resolved from benzo[*ghi*]perylene-d_{14} and benzo[*ghi*]perylene (peaks in front and after dibenz[*a,h*]anthracene, respectively), which are present in small amounts in the five aromatic ring *cata*-condensed isomer fraction. The picene peak has an obvious tailing shoulder. These coelutions were not apparent using the 3 μm column for the analysis of the 278 molecular

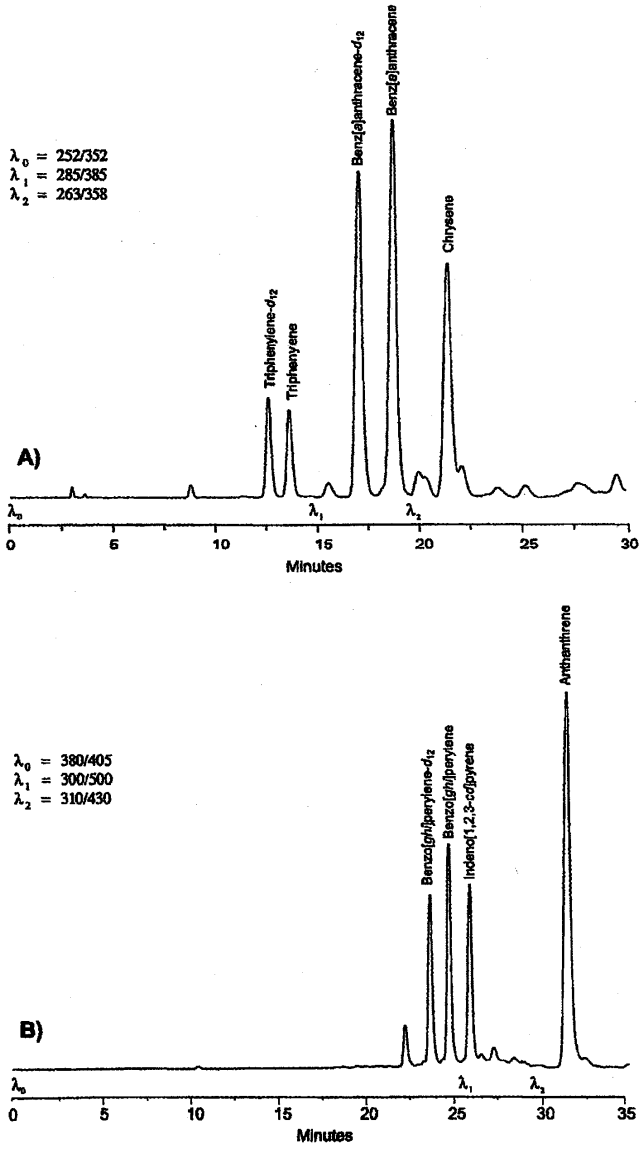

FIGURE 5 Reversed-phase LC-FL analysis of isomer fractions isolated from SRM 1649a. (A) four aromatic ring fraction, and (B) six aromatic ring fraction.

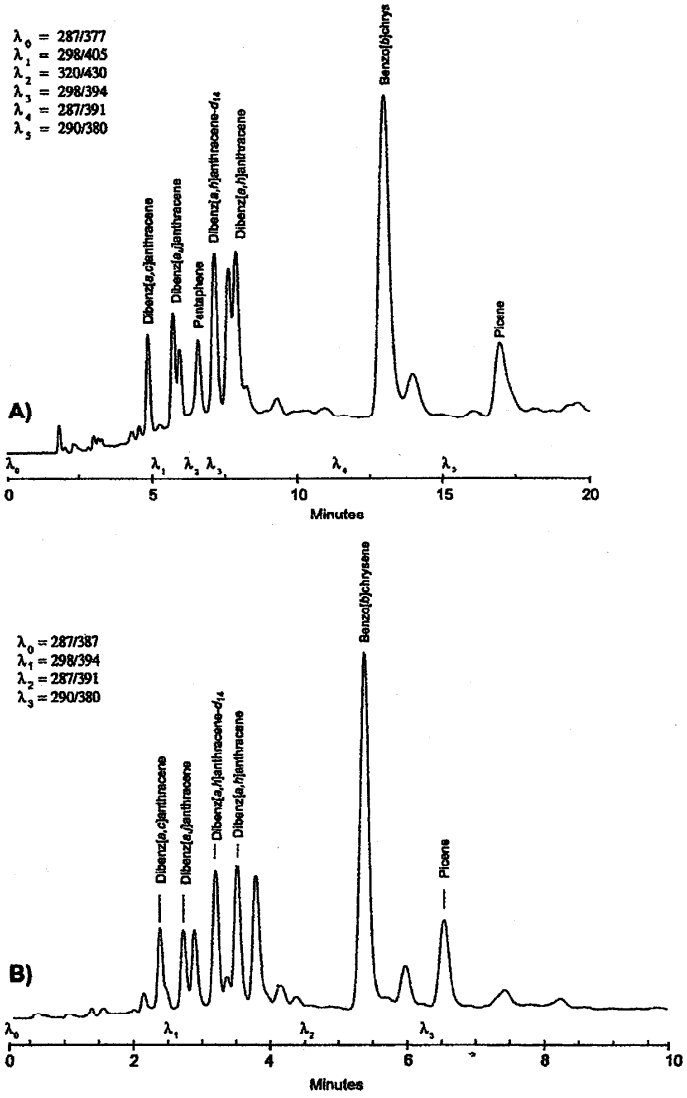

FIGURE 6 Reversed-phase LC-FL analysis of the five aromatic ring isomer fractions isolated from SRM 1649a. (A) 5 µm particle-size column, and (B) 3 µm particle-size column.

weight fraction (see Fig. 6B). Therefore, the results for all of the isomers (except pentaphene which was only determined on the 5 μm column) were used from the 3 μm column, and only the results for the three completely resolved isomers were used from the 5 μm column for certification measurements. The differences in the resolution of components using the two columns is probably due more to the selectivity differences of the two polymeric C_{18} columns [65] rather than the increased efficiency of the smaller particle column. The 5 μm column used for the separation of this isomer fraction had a high phase loading as defined by the $\alpha_{TBN/BaP} = 0.46$ [50], whereas the 3 μm column was a more typical phase loading with $\alpha_{TBN/BaP} = 0.65$ [65].

Perdeuterated PAHs were used as internal standards for both the LC-FL and GC/MS methods as summarized in Table I. In many cases different perdeuterated PAHs were used in the various methods for the quantification of a particular PAH, thereby providing additional independence in the methods. For the LC-FL methods results determined by different internal standards were often compared. For example, the results for perylene, benzo[*k*]fluoranthene, and benzo[*a*]-pyrene using the 5 μm column were calculated using both benzo[*a*]-pyrene-d_{12} and perylene-d_{12} and the results were found to be 14% lower using the perylene-d_{12}. Examination of the benzo[*a*]pyrene-d_{12} revealed a small shoulder, which may account for this difference; thus the results calculated using the perylene-d_{12} as internal standard were used for the determination of the certified value.

Comparison of GC/MS and LC Results

When the results from the seven data sets in Table II are compared, they are found to be in good agreement. The range of the results for the seven data sets was typically between 8% to 16%, with some as low as 4% (fluoranthene and benzo[*k*]fluoranthene) and two as high as 47% and 54% (benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene, respectively). For the isomers that are not separated by all the techniques, the agreement is excellent between the combined results and the sum of the individually measured isomers. For example, the sum of the individual results for chrysene and triphenylene, *i.e.*, 4.35 mg/kg for GC/MS (Sm) and 4.47 mg/kg for LC-FL (Fraction), agree well with the mean of the four other GC/MS data sets (4.41 mg/kg) where the two isomers are not

separated. For the benzofluoranthene isomers the addition of GC/MS results from the 50% phenyl methylpolysiloxane provides individual values for each isomer for comparison with GC/MS results from the liquid crystalline phase and LC-FL results. For the benzo[*b*]fluoranthene and benzo[*j*]fluoranthene, which coelute on the 5% phenyl methylpolysiloxane phase (GC/MS I, II, and III), the mean value of 7.41 mg/kg (GC/MS I, II, and III) is in good agreement with the sum of the individual values determined on the 50% phenyl methylpolysiloxane, 7.50 mg/kg [GC/MS (IV)], and the value determined by GC/MS on the smectic liquid crystalline column, 7.72 mg/kg. Three sets of results for the individual measurement of dibenz[*a*, *h*]anthracene and dibenz[*a*, *c*]anthracene are available which provide a mean value of the sum of the two isomers of 0.488 mg/kg compared to the mean of the three data sets determined on the 5% phenyl methylpolysiloxane phase, 0.416 mg/kg, where the two isomers coelute.

Determination of the Certified and Reference Concentrations

The results of the various methods summarized in Table II were combined to determine certified values for 22 PAHs, which are provided in Table IV. The certified values are the equally-weighted means of from two to five of the different method results from Table II combined using the approach described by Schiller and Eberhardt [67] and described in detail previously for PAHs in a sediment SRM [7]. The uncertainty associated with the certified value is an expanded uncertainty at the 95% level of confidence which includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study. The expanded uncertainty defines a range of values for the certified value within which the true value is believed to lie at a level of confidence of approximately 95%. The uncertainties of the certified values range from a low of 1.6% for benzo[*k*]fluoranthene to 23% for benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, and pentaphene, and the relative uncertainties for 14 of the 22 PAHs were less than 10% (8 were less than 5%) and only 3 PAHs had uncertainties greater than 20%.

Reference concentrations were determined for 23 additional PAHs and are summarized in Tables V and VI. Reference values are noncertified values that are the best estimate of the true value; however, the

TABLE IV Certified concentrations for selected PAHs in SRM 1649a, Urban Dust

	Concentration (mg/kg dry-mass basis)[a,b]	*Percent relative uncertainty*
Phenanthrene[c,d,e,f]	4.14 ± 0.37	(± 8.9%)
Anthracene[c,d,e,f]	0.432 ± 0.082	(± 19%)
Fluoranthene[c,d,e,f]	6.45 ± 0.18	(± 2.7%)
Pyrene[c,d,e,f]	5.29 ± 0.25	(± 4.8%)
Benz[*a*]anthracene[c,d,g]	2.21 ± 0.073	(± 3.3%)
Chrysene[e,g]	3.049 ± 0.060	(± 2.0%)
Triphenylene[e,g]	1.357 ± 0.054	(± 4.0%)
Benzo[*b*]fluoranthene[e,f,g]	6.45 ± 0.64	(± 9.9%)
Benzo[*k*]fluoranthene[c,d,e,f,g]	1.913 ± 0.031	(± 1.6%)
Benzo[*a*]fluoranthene[c,d,e]	0.409 ± 0.035	(± 8.6%)
Benzo[*e*]pyrene[c,d,e,g]	3.09 ± 0.19	(± 6.3%)
Benzo[*a*]pyrene[c,d,e,f,g]	2.509 ± 0.087	(± 3.5%)
Perylene[c,d,e,f,g]	0.646 ± 0.075	(± 11%)
Anthanthrene[c,d,e,g]	0.450 ± 0.067	(± 15%)
Benzo[*ghi*]perylene[c,d,g,h,i]	4.01 ± 0.91	(± 23%)
Indeno[1,2,3-*cd*]pyrene[c,d,g,h,i]	3.18 ± 0.72	(± 23%)
Dibenz[*a,j*]anthracene[c,d,g,h]	0.310 ± 0.034	(± 11%)
Dibenz[*a,c*]anthracene[e,g,h]	0.200 ± 0.025	(± 13%)
Dibenz[*a,h*]anthracene[e,g,h]	0.288 ± 0.023	(± 8.0%)
Pentaphene[c,d,g,h]	0.151 ± 0.035	(± 23%)
Benzo[*b*]chrysene[c,d,e,g,h]	0.315 ± 0.013	(± 4.1%)
Picene[c,d,e,g,h]	0.426 ± 0.022	(± 5.1%)

[a] Concentrations reported on dry-mass basis; material as received contains approximately 1.2% moisture.
[b] Each certified value is the equally-weighted mean of the means from two or more independent analytical methods. Each uncertainty, computed according to the CIPM approach as described in the ISO Guide [67], is an expanded uncertainty at the 95% level of confidence, which includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study. The expanded uncertainty defines a range of values for the certified value within which the true value is believed to lie, at a level of confidence of approximately 95%.
[c] GC/MS (I) analysis.
[d] GC/MS (II) analysis.
[e] GC/MS (Sm) analysis.
[f] LC-FL analysis of total PAH fraction.
[g] GC/MS (III) analysis.
[h] LC-FL analysis of isomeric PAH fractions.
[i] GC/MS (IV) analysis.

values do not meet all the criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods. For the PAHs listed in Table V, the reference concentration values are based on measurements by one to three of the GC/MS method shown in Table II. When results are available from only one method, the values obviously do not meet the certification criteria of "two or more independent methods" and are provided as reference concentrations.

TABLE V Reference concentrations for selected PAHs in SRM 1649a, Urban Dust[a, b]

	Concentration mg/kg dry-mass basis
Fluorene[c]	0.23 ± 0.05
Dibenzothiophene[d]	0.18 ± 0.01
1-Methylphenanthrene[c, d, e]	0.37 ± 0.04
2-Methylphenanthrene[c, d, e]	0.73 ± 0.12
3-Methylphenanthrene[c, d, e]	0.50 ± 0.05
4-Methylphenanthrene and 9-Methylphenanthrene[c, d, e]	0.34 ± 0.01
2-Methylanthracene[c, d, e]	0.09 ± 0.03
4H-Cyclopenta[*def*]phenanthrene[c, d, e]	0.32 ± 0.06
Benzo[*c*]phenanthrene[d, e]	0.46 ± 0.03
Benzo[*ghi*]fluoranthene[d]	0.88 ± 0.02
Benzo[*j*]fluoranthene[d, f]	1.5 ± 0.4
Indeno[1,2,3-*cd*]fluoranthene[e]	0.23 ± 0.01
Benzo[*c*]chrysene[d]	0.080 ± 0.004

[a] Concentrations reported on dry-mass basis; material as received contains approximately 1.2% moisture.
[b] The reference value for each analyte is the equally-weighted mean of the means from two or more analytical methods or the mean from one analytical technique. The uncertainty in the reference value defines a range of values that is intended to function as an interval that contains the true value at a level of confidence of 95%. This uncertainty includes sources of uncertainty within each analytical method, among methods, and from the drying study.
[c] GC/MS (I) analysis.
[d] GC/MS (Sm) analysis.
[e] GC/MS (II) analysis.
[f] GC/MS (III) analysis.

TABLE VI Reference concentrations for selected PAHs in SRM 1649a, Urban Dust, as determined by LC

	Concentration µg/kg dry-mass basis[a, b, c]
Dibenzo[*a, e*]pyrene	630 ± 80
Dibenzo[*a, h*]pyrene	53 ± 2
Dibenzo[*a, i*]pyrene	130 ± 10
Dibenzo[*b, k*]fluoranthene	800 ± 100
Naphtho[2,3-*a*]pyrene	57 ± 5
Naphtho[2,3-*e*]pyrene	240 ± 30
Naphtho[2,3-*b*]fluoranthene	230 ± 20
Naphtho[1,2-*k*]fluoranthene	550 ± 60
Naphtho[2,3-*k*]fluoranthene	57 ± 3

[a] Concentrations reported on dry-mass basis; material as received contains approximately 1.2% moisture. Note that the concentrations are in µg/kg whereas the concentrations in Tables II, IV, V, and VII are in mg/kg.
[b] Expanded uncertainties are sample standard deviations of the mean concentrations.
[c] Concentrations reported by Wise *et al.* [53] were determined using LC-fluorescence analysis of isomeric PAH fractions; duplicate analyses of two sample extracts.

However, many of the values for PAHs in Table V are based on results from two or three methods. In these cases the values are not considered as certified because of insufficient agreement of the methods (*e.g.*, benzo[*j*]fluoranthene), insufficient independence of the methods, or insufficient information on the purity of reference compounds used for calibration (*e.g.*, the methylphenanthrenes). The results for nine dibenzopyrene and dibenzofluoranthene isomers in Table VI were determined by the LC-FL (Isomer Fraction) method and were reported previously [31]; however, these results were evaluated during the recertification process to become reference values. These results represent the first reported reference values for high molecular weight PAHs in any natural matrix SRMs. The 44 certified and reference values for PAHs in SRM 1649a represent the largest number of PAH reported in a natural matrix SRM.

Comparison of SRM 1649a with SRM 1649

The recertification of SRM 1649 provided an excellent opportunity to evaluate the stability of the air particulate material after a period of about 17 years. In the original certification in 1982 only five PAHs were certified with measurement results reported for an additional nine PAHs, which under the current modes of certification [15] would be designated as reference values. The results of the original certification (SRM 1649) are compared with the results of the recertification (SRM 1649a) in Table VII for the 14 PAHs measured in the original SRM 1649. Table VII also includes the percent difference between the SRM 1649 and 1649a results and an indication (designated with an *X* in the final column) of whether the uncertainties on the "new" and "old" certified values overlap. As shown in Table VII, all the values for the original five PAHs with certified values have decreased from 4% to 15%; the remaining noncertified values have also decreased from 4% to 30% with the exception of benzo[*b*]fluoranthene which increased by 4%. However, the decreases greater than 15% can usually be attributed to improvements in the analytical methodology for these specific PAHs. For example, the original LC-FL measurements of dibenz[*a*, *h*]anthracene were made with no cleanup of the extract, whereas the recent measurements were performed on the normal-phase LC-isolated 278 molecular weight isomer fraction, which would

TABLE VII Comparison of concentrations for selected PAHs in SRM 1649a *vs.* SRM 1649[a,b]

	SRM 1649a[a] *mg/kg (dry-mass basis)*		*SRM 1649*[b] *mg/kg (as received basis)*		*Percent difference*[c]	*Overlap of uncertainty*[d]
Phenanthrene	4.14 ± 0.37		(4.5 ± 0.3)		−8%	*X*
Fluoranthene	6.45 ± 0.18	(± 2.7%)[e]	7.1 ± 0.5	(± 7%)[g]	−9%	*X*
Pyrene	5.29 ± 0.25		(7.2 ± 0.2)[f]		−27%	
			(6.3 ± 0.4)[g]		−16%	
Benz[*a*]anthracene	2.21 ± 0.073	(± 3.3%)	2.6 ± 0.3	(± 12%)	−15%	
Chrysene	3.049 ± 0.060		(3.5 ± 0.1)		−13%	
Triphenylene	1.357 ± 0.054		(1.7 ± 0.1)		−20%	
Benzo[*b*]fluoranthene	6.45 ± 0.64		(6.2 ± 0.3)		+4%	*X*
Benzo[*k*]fluoranthene	1.913 ± 0.031		(2.0 ± 0.1)		−4%	*X*
Benzo[*e*]pyrene	3.09 ± 0.19		(3.3 ± 0.2)		−6%	*X*
Benzo[*a*]pyrene	2.509 ± 0.087	(± 3.5%)	2.9 ± 0.5	(± 17%)	−13%	*X*
Perylene	0.646 ± 0.075		(0.84 ± 0.09)[f]		−19%	
			(0.65 ± 0.02)[g]		0%	*X*
Benzo[*ghi*]perylene	4.01 ± 0.91	(± 23%)	4.5 ± 1.1	(± 24%)	−11%	*X*
Indeno[1,2,3-*cd*]pyrene	3.18 ± 0.72	(± 23%)	3.3 ± 0.5	(± 15%)	−4%	*X*
Dibenz[*a,h*]anthracene	0.288 ± 0.023		0.41 ± 0.07		−30%	

[a] See footnote b in Table IV for description of certified value and uncertainty.
[b] The certified value and the estimated uncertainty listed for a constituent are contained in the union of 95% confidence intervals computed separately for each method and represent an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material inhomogeneity. The estimated uncertainty is intended to correspond to approximately 95% confidence limits [16]. The concentration values for SRM 1649 in parentheses are noncertified values.
[c] Percent difference in the original certified values for SRM 1649 and the certified values for the reissue as SRM 1649a.
[d] Overlap of uncertainties associated with the certified values or, in the case of the noncertified values for SRM 1649, overlap of the measurement uncertainties.
[e] Values in parentheses are the percent relative uncertainty of the certified values for the PAHs that were certified in the SRM 1649.
[f] Result determined by GC-FID.
[g] Result determined by LC-FL.

produce a more reliable result. In the case of the original triphenylene measurements, the concentration was determined without the addition of an internal standard, whereas the recent measurements were quantified based on using triphenylene-d_{12} as the internal standard, which had been added prior to extraction and cleanup and therefore should mimic the behavior of triphenylene and provide a more reliable result. In the original Certificate of Analysis, results were reported for pyrene and perylene from two analytical techniques (GC-FID and LC-FL); however the two results were not in agreement, with the LC-FL result lower by 15% and 29%, respectively. Subsequent analyses of SRM 1649 and the comparison of results of LC and GC/MS analyses on other environmental matrix SRMs performed shortly thereafter [29] indicated that the original GC-FID values for pyrene and perylene were overestimated and the LC-FL results were considered as more accurate. Thus it appears that 4% to 15% is a realistic value for the decrease in the measured concentrations of SRM 1649 between the original certification and the recertification analyses.

This decrease in the concentrations may indicate that the air particulate material has changed during the past 17 years or perhaps the decrease is just an artifact of the improvement in the measurements. The air particulate material has been stored at room temperature in amber glass bottles since the original measurements. The decrease is actually slightly more ($\sim$1%) because the original measurements were reported on an as-received basis whereas the new certified values are reported on a dry-mass basis. Even though the five original certified values have decreased, the new certified values are, with the exception of benz[*a*]anthracene, still within the uncertainties of the original certified values. When the uncertainties of the new certified values and the uncertainties of the old certified values (or the measurement uncertainties of the noncertified values) are considered, 9 of the 14 concentration values overlap. The fact that all of the values decrease suggest that the material has changed. However, all of the analytical methods used in the recertification are more selective relative to cleanup and isolation of the PAH fraction and they are more selective in detection for the GC methods (*i.e.*, MS *vs.* FID), which would tend to produce lower values. Thus, it is difficult to determine definitively whether the material has been stable with respect to the PAH concentrations over the past 17 years.

Additional Information on SRM 1649a

In addition to the certified and reference values for 44 PAHs, the Certificate of Analysis [50] for SRM 1649a also provides certified values for 35 polychlorinated biphenyl congeners and 8 chlorinated pesticides as described by Poster *et al.* [51]. Reference values are provided for 32 inorganic constituents, mutagenic activity [38, 50], particle-size characteristics, total organic carbon, total extractable material, and carbon composition. The carbon composition values include the results from both NIST and other laboratories using various techniques for total carbon, insoluble carbon, organic carbon, elemental carbon, pyrolyzed carbon, and carbonate carbon. Reference values are also provided for the 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners (17 individual congeners) and total tetra-, penta-, hexa-, and hepta-congeners of polychlorinated dibenzo-*p*-dioxin and dibenzofuran as determined from an interlaboratory comparison exercise among 14 laboratories [68]. With a total of over 160 certified and reference values for constituents or properties, SRM 1649a is the most extensively characterized natural environmental matrix SRM available from NIST.

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Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials are the best available for the purpose.

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